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EFFICIENCIES OF ORANGE AND LEMON PEEL IN THE REMOVAL OF DYE FROM TEXTILE INDUSTRY EFFLUENT

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ABSTRACT

Use of various dyes in order to color the products is a common practice in composite textile industry. The presence of these dyes in water even at low concentration is highly visible and undesirable. This comparative study was carried out for the utilization of orange peel and lemon peel as adsorbent for the removal of dyes from wastewater and to establish it as a standard wastewater treatment process for textile industry. This experiment was performed in the laboratory scale and batch adsorption studies were conducted. The raw materials were obtained and treated for the removal of dyes at different dosages. The use of cheap and ecofriendly adsorbents were studied in this paper as an alternative substitution of activated carbon for removal of dyes from textile industry effluent. Adsorbents prepared from orange peel and lemon peel which are domestic wastes which are easily available were successfully tested and used to remove the dye, methylene blue from an aqueous solution in a batch wise column. This study investigates the potential use of natural materials namely, orange peel and lemon peel pretreated with nominal treatment method, for removal of methylene blue from simulated wastewater. Treated orange peel and lemon peel were used to study the adsorbtion methylene blue at varies dosages.

KEYWORDS: dye removal; textile industry; methylene blue; wastewater; adsorbtion; orange peel; lemon peel;UV Visile sprectrometer

I. INTRODUCTION:

The presence or introduction of unwanted materials in the environment which have harmful or poisonous effects is called Pollution. With the advancement in technology, the luxury of human life has enhanced considerably and so has the degradation of ecological systems. Instance of such advancement is the use of dyes in various fields of textiles, food, cosmetics, paper, paints, pharmaceuticals and several other industries. Most synthetic dyes are aromatic in nature which makes them physically, chemically, thermally, biologically and optically stable [1]. Upon degradation, the dye products are toxic, carcinogenic and mutagenic to life forms .The effluents containing dyes are difficult to be treated because of high chemical oxygen demand, color of the water which is easily recognizable and high structural stability of these molecular dyes. Numerous studies have been conducted to assess the harm impacts of colorants on the ecosystem. A variety of physical, chemical and biological treatment methods have been reported. The choice of method is limited by cost, efficiency, release of secondary effluents and simplicity in design for operation. Among the treatment methods, adsorption is the most preferred method because it is simple & efficient [5]. The commercially available granulated activated carbon provides an excellent adsorption surface but is expensive. Natural materials that are available in large quantities may have high adsorption potential as an inexpensive adsorbent.

II. ADSORPTION AND IT'S TYPES:

Adsorption is the process in which matter is extracted from one phase and concentrated at the surface of a second phase (Interface accumulation). This is a surface phenomenon The adsorption process is used to remove colour and other soluble organic pollutants from effluent [1]. The process also removes toxic chemicals such as pesticides, phenols, and organic dyes that cannot be treated by conventional treatment methods [2]. Dissolved organics are adsorbed on the surface when waste water containing these are made to pass through adsorbent. Most commonly used adsorbent for treatment is activated carbon.. The pores need to be large enough for soluble organics compounds to diffuse in order to reach the abundant surface area.

A. **Exchange adsorption (ion exchange):** Electrostatic due to charged sites on the surface. Adsorption goes up as ionic charge goes up and as hydrated radius goes down.

B. **Physical adsorption:** Van der Waals attraction between adsorbate and adsorbent. multilayer adsorption. The attraction is not fixed to a specific site and the adsorbate is relatively free to move on the surface.

C. **Chemical adsorption:** Some degree of chemical bonding between adsorbate and adsorbent characterized by strong attractiveness. Adsorbed molecules are not free to move on the surface.

Some of the common adsorbents are described below:

i. **Activated carbon:**
The adsorption properties of carbon-rich materials like wood charcoal have been improved by special activation processes. Activated carbons can be produced from different carbon-containing raw materials like wood, wood charcoal, coconut shells, and sawdust. For organic raw materials like wood, a preliminary carbonization process is necessary to transform the cellulose structures into a carbonaceous material [3].

ii. **Polymeric adsorbents:**
Polymeric adsorbents, also referred to as adsorbent resins, are porous solids with considerable surface areas and distinctive adsorption capacities for organic molecules. They are produced by copolymerization of styrene, or sometimes also acrylic acid esters, with divinylbenzene as a cross-linking agent [2].

iii. **Natural and low-cost adsorbents:**
Among the natural and low-cost adsorbents, clay minerals are important. Their adsorption properties are related to the net negative charge of the mineral structure. This property allows clays to adsorb positively charged species – for heavy metal cations such as Cu^{2+}, Zn^{2+} etc. [2]. Relatively high adsorption capacities were also reported for organic dyes during treatment of textile wastewater.

III. MATERIALS USED IN THE EXPERIMENT:

i. **Orange peel and lemon peel:**
The natural adsorbents used in the present work are dried peels of lemon and orange. The materials are easily available and natural. They also act as cheap adsorbents due to the presence of large no of pores. These materials are pollution free and eco – friendly [3].

ii. **Methylene blue:**
Adsorbates are substances which are adsorbed or removed. They mainly include colour dye and dissolved solids. The adsorbate removed here is methylene blue dye.

Methylene blue (MB) is a cationic dye and is regarded as significant threat to human and eco system due to its carcinogenic and mutagenic properties that forms a deep blue solution when dissolved in water [3]. Methylene blue has been widely used in coloring paper, wools, as biological stains and dying cottons. It is a heterocyclic aromatic chemical compound with the chemical formula $C_{16}H_{18}N_3Cl$. Though MB is not strongly hazardous it can cause some harmful effects [1]. It can cause eye injury to both human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, profuse sweating, diarrhea, gastritis, mental confusion and methemoglobinemia. Acute exposure to methylene blue can cause increased heart rate, vomiting, and tissue necrosis in humans. Fig. 1 shows the molecular structure of MB.

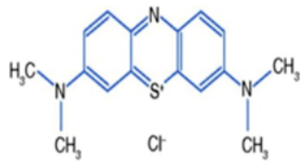

Fig. 1: Molecular structure of Methylene Blue

1. **Model water:**
Wastewater which was used in the experiments was prepared by dissolving methylene blue in distilled water concentration 2.5 ppm. A stock solution of methylene blue dye was prepared by dissolving 0.1 g of dye powder in 100 water (1000 ppm).The batch adsorption studies were carried out by preparing various concentration of 0.5ppm, 1ppm, 1.5ppm, 2ppm, 2.5ppm and the calibration was carried out. The concentrations of residual MB dye were measured using UV visible spectrophotometer equipment at 664 nm. The aqueous solutions of varied concentrations of methylene blue dye were prepared by dilution from its stock solution and the studies were done by varying different parameters. The stock solution prepared for the study is shown in Fig. 2.

Fig. 2: Methylene blue stock solution

2. **Ultra – Violet Visible Spectrometer:**
Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved [2]. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state. Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons, the longer the wavelength of light it can absorb [4]. The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. The radiation source is often a Tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm), Xenon arc lamp, which is continuous from 1602,000 nm; or more recently, light emitting diodes (LED) for the visible wavelengths. Fig. 3 represents a double beam Ultra – Violet Visible Spectrometer

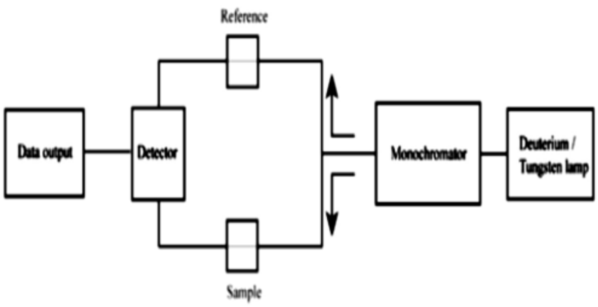

Fig. 3: Schematic of a double beam Ultra – Violet Visible Spectrometer

4. **Preparation of lemon and orange peel:**
Orange and lemon are used mainly in soft drinks industries all over the world. They discard a huge amount of orange peels. At first, the peels were cleaned with distilled water to remove dust particles and water-soluble impurities. The peels were dried in sunlight for 2 days and kept in oven for 8 hours. After drying, the pieces were crushed in a mixer grinder until they became fine powder. Finally the orange peel powder was stockpiled in air tight packets so that they can be used in future without any further treatment [5]. The orange peel should be thoroughly washed and dried properly or else it imparts colour after removal of methylene blue and leads to adverse result and increase in chemical oxygen demand (COD) [6]. Fig. 4 shows the lemon and orange peels used as adsorbents.

Fig. 4: Orange and lemon peel samples

V. EXPERIMENTAL PROCEDURE:

1. **Calibration of Methylene Blue:**
Stock solution of methylene blue was prepared by taking 0.1g of dye powder in standard flask and diluted to 100 ml (1000ppm). After that take 1 ml of stock solution in measuring jar and diluted to 100 ml (10ppm) and was kept as a working standard for calibration. Take adsorbate concentration as 0.5 ppm, 1ppm, 1.5ppm, 2ppm and 2.5ppm.Each of the sample was detected in spectrometer and the calibration graph was plotted [4]. From the graph a suitable concentration was chosen for further adsorption batch studies.

2. **Adsorption of methylene blue using orange peel:**
The adsorption of methylene blue dye using orange peel powder was studied using the batch techniques. To assess the removal efficiency of orange peel under various adsorbent dosages, methylene blue standard sample in the range 2.5 ppm was prepared by taking appropriate quantities of standard methylene blue solution with distilled water. The experiments were conducted in 250 ml Erlenmeyer flasks containing different amount of bio adsorbents 0.2g, 0.4g, 0.6 g, 0.8g, 1g, 1.4g, 1.8g, 2.2g, 2.4g and 100ml of MB solution at desired concentrations (2.5ppm). First the stock solution was prepared from which 25ml was taken and balance 75ml was added to prepare the solution of required concentration for batch adsorption study. The various doses of orange ranging from 0.2g to 2.4g were added in the flask containing methylene blue solution. The flasks were agitated using a shaker at 150rpm for different time intervals. After agitation allow the sample to settle and is filtered using filter paper & residual MB concentration using UV visible spectrometer at 664nm is determined. Based on various studies conducted, colored particles have the property of absorbing light in visible region [4]. Here methylene blue particles absorb radiation of 664nm. Here the monochromatic source is emitted from monochromator and strikes the particles and sends it to photo detector. The results obtained from the spectroscopy confirmed that the considerable amount of dye was adsorbed on adding orange peel powder. Absorbance readings were compared with standard curve [6].

The same procedure was repeated with lemon peel samples.

Fig. 5: Samples prepared for batch adsorption studies

3. **Chemical Oxygen Demand (COD) Analysis:**
The COD determination is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. It is an important, rapidly measured parameter for industrial waste water studies and for control of waste water treatment pro-

cess. So we have to analyze the COD before and after adsorption using orange and lemon peel.

The reagents used are Potassium dichromate, Sulphuric acid

Silver sulphate, Mercuric sulphate, Ferroin indicator and organic free distilled water.

3. a. Procedure:

- Take 10 ml samples of methylene blue, maximum adsorbent capacity dosage samples of lemon & orange peel & blank sample in 250 ml of refluxing flask.
- Add 0.1g of mercuric sulphate, 5 ml of potassium dichromate by pipette, 14 ml of concentrated sulphuric acid reagent by measuring cylinder.
- Acid should be added in controlled manner with mixing of the sample. If the sample color changes to green, dilute the sample and repeat the procedure for diluted sample. Connect the reflux flask through the condenser and reflux for a minimum period of 2hrs at 150°C.
- After that the condenser is taken out and cooled as room temperature. It is then titrated with standard 0.1 N ferrous ammonium sulphate using 2 to 4 drops of ferroin indicator.
- Let the titrate value be 'A' End point is the sharp color change from blue green to brick red, even though blue green reappears within minutes.
- Let the titrate value be 'V' ml. In same manner, a blank with distilled water 10 ml and follow the procedure from previously. Let the titrate value be 'B' ml. Calculate the COD (mg/l) as follows:

COD = (B-A) xNx8000/V mg/l

where, B = ml of ferrous ammonium sulphate used for titrating against blank.

A = ml of ferrous ammonium sulphate used for titrating against sample

N = Normality of ferrous ammonium sulphate.

V = Volume of sample used

VI. RESULTS AND DISCUSSIONS:

1. **Effect of adsorbent dosage (orange peel):**
Adsorbent dose represents an important parameter due to its strong effect son the adsorption capacity of an adsorbent on given initial concentration of adsorbate. Effect of adsorbent dose on removal of MB was monitored by varying adsorbent dose from 0.2 g/100ml to 2.4g/100ml at different PH. It was seen that the removal of methylene blue increases with an increase in the amount of adsorbent used. For all the experiments, initial MB concentration was fixed at 2.5 mg/l. At low amount of dosage higher uptake was obtained.

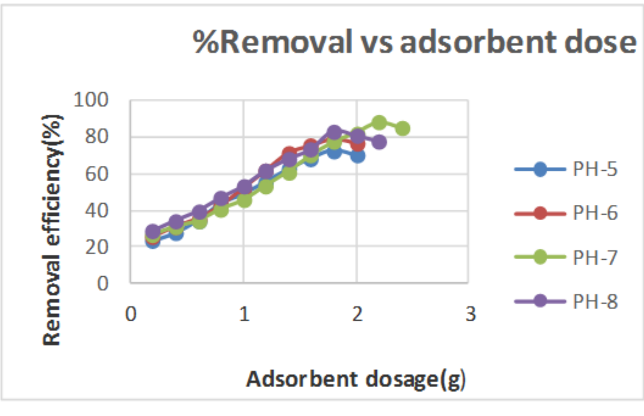

Fig. 6: Graph showing efficiency vs dosage for orange

2. **Optimal contact time for adsorbent dosages (orange peel):**
The removal efficiency is increases with increase in contact time between adsorbate and adsorbent. It can be attributed to the fact that more time becomes available for the dye to make an attraction complex with orange peels. The graph shows that, Initial removal occurs rapidly as soon as the dye and peels in contact but after that when some of the easily available active sites engaged, dye needs time to find out more active sites for building.so, removal percentage is increased steadily over the period of experiment . It is concluded that dye and peels should be in contact for 120 minutes in order to get maximum removal percentage as shown in Fig.7

3. **Effect of adsorbent dosage (lemon peel):**
Adsorbent dose represents an important parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of adsorbate. Effect of adsorbent dose on removal of MB was monitored by varying adsorbent dose from 0.2g/100ml to 2.4g/100ml. It was seen that the removal of methylene blue increases with an increase in an amount of adsorbent and reached on equilibrium value after 1.6g of absorbent of PH-7. For all the experiment, initial MB concentration was fixed at 2.5 mg/l. The most important factors is that adsorption site remains unsaturated during the adsorption reaction. The decrease in adsorption capacity with increase in adsorbent dose is mainly attributed to non-saturation of the adsorption sites during the adsorption process as shown in Fig.8.

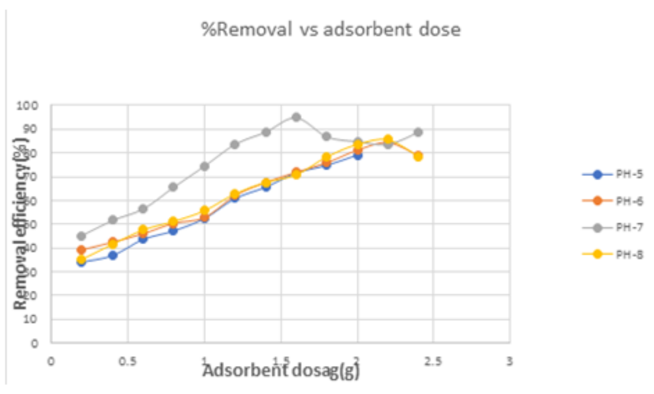

Fig. 8: Graph showing efficiency vs dosage for lemon peel

4. **Optimal contact time for adsorbent dosages (lemon peel):**
In the case of lemon peel the contact time is less than the orange peel Initial removal occurs rapidly as soon as the dye and peels come in contact but after that when some of the easily available active sites engaged by dye needs time to find out more active sites for building. Removal percentage is increased steadily over the period of experiment .It is concluded that dye and peel should be in contact for 120 minutes in order to get maximum removal percentage as shown in Fig. 9.

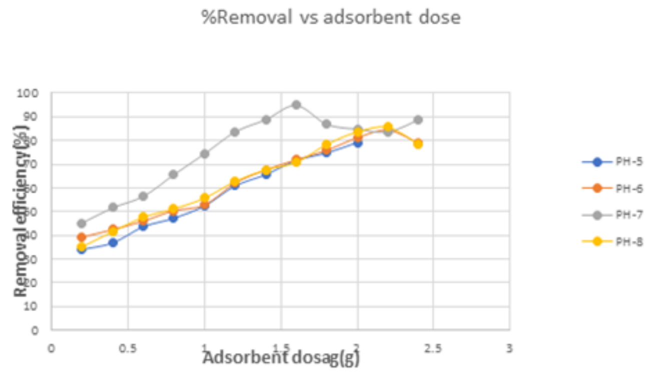

Fig. 9: Effect of contact time on the removal of dye by adsorption

5. **Results of COD Analysis:**
The analysis the COD before and after adsorption using orange & lemon peel was done. In the result, MB dye shown a COD content of 16 mg/l. After using orange peel as an adsorbent there was no reduction in the COD content. In the case of lemon peel as an adsorbent there was a reduction in the COD value compared to orange peel. So that in the COD analysis, lemon peels as an adsorbent was effective in the reduction of COD.

Material	Volume of sample (ml)	A (Sample) ml	B (Blank) ml	COD (mg/l)
Methylene Blue	10	13.1	13.3	16
Orange Peel	10	12.8	13.3	40
Lemon Peel	10	13.2	13.3	8

VII. CONCLUSION:

Removal of methylene blue dye from aqueous solution using orange peel &

lemon peel was done and following conclusion were arrived:

- Lemon peel was found to have better adsorbing capacity than orange peel
- The adsorption of dyes onto orange peel & lemon peel are influenced by amount of adsorbents, pH and contact time. As adsorbent dose increases adsorption increases due to the availability of free sites. As we increase adsorbent dose more than the optimum, the removal efficiency decreases.
- Removal of methylene blue from textile wastewater by adsorption on lemon peels has been found to be useful than orange peel for controlling water pollution due to dyes.
- In COD analysis lemon peel was found to reduce COD and has higher adsorption capacity, hence found superior.
- The permissible exposure of methylene blue is 0.4ppm and the after adsorption solution contained only 0.13ppm of methylene blue, thus it is safe to dispose into the environment.

Based on the present study it can be concluded that the use of the lemon peel powder as bio adsorbent for removal of methylene blue is feasible and the removal by adsorption increases with increase in adsorbent dose. After optimum dosage the removal efficiency decreases. In these study adsorbent dosage (orange & lemon) increases from 0.2g to 2.4 g per 100 ml of 2.5 ppm concentrated methylene blue solution. Optimum dosage obtained is 2.2 g and maximum efficiency is88.4 % in orange peel and optimum dosage obtained is 1.6 g and maximum efficiency is 94.8% in lemon peel. Results confirm that the adsorption is a very effective process for the decolourisation of wastewater. Thus it can be concluded that lemon peel is better than orange peel for the removal of methylene blue dye from waste water.

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